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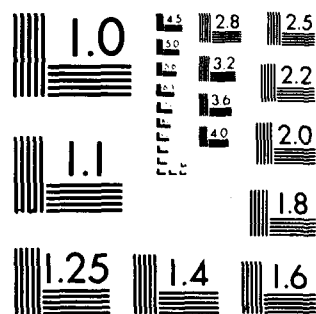
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BY

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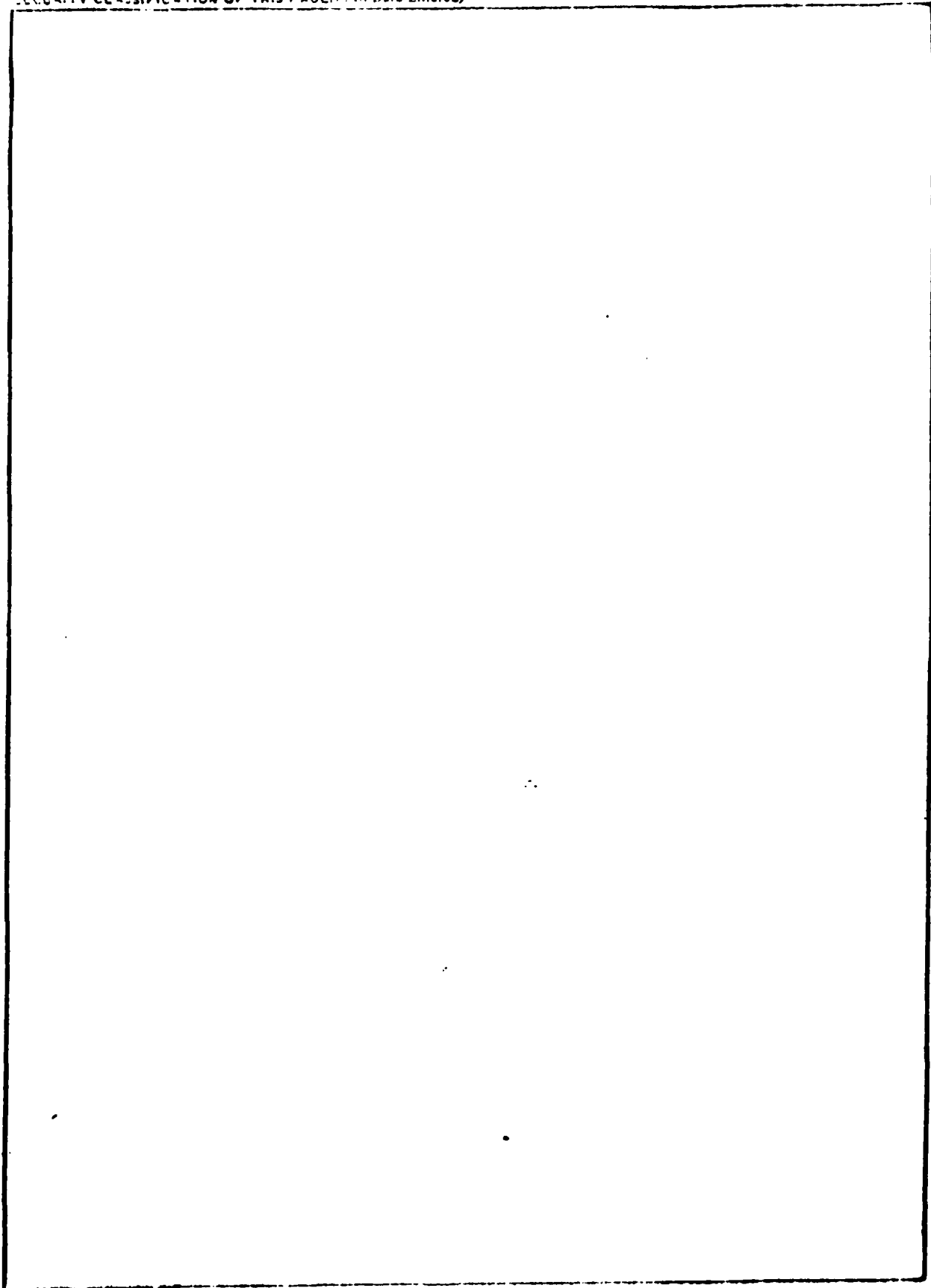
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The solvent dependence of metallophthalocyanine redox equilibria is reported for manganese, iron and cobalt phthalocyanines in dimethylacetamide, dimethylsulfoxide and in pyridine. Considerable sensitivity is observed with iron and cobalt; much less with manganese. Both positive and negative deviations of redox potentials with solvent donicity (as defined by the Gutmann solvent donicity scale) are observed and explained, in terms of coordination number, spin state and the nature of the metal ligand bond. Comparison is made with analogous porphyrin derivatives.		

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## SOLVENT DEPENDENCE OF PHTHALOCYANINE REDOX EQUILIBRIA

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Canada, M3J 1P3.

The phthalocyanines and porphyrins represent a unique series of complexes which can be varied almost inexhaustively via change of substituent, metal ion, axial ligand, spin state and coordination number, yet retain the basic  $MN_4$  unit. Detailed analysis of the variation of redox equilibria with each of these factors provides rare insights into the nature of metal ligand binding. Such data are therefore of fundamental value in the development of coordination chemistry, and in the elucidation of the redox (electron transfer, oxygen binding) roles played by metal ions in biological systems.

During recent years, there has been extensive study of the redox equilibria exhibited by metalloporphyrin derivatives [e.g. 1 - 16], but less has appeared concerning the behaviour of the metallophthalocyanines [17 - 24]. We present here a preliminary detailed comparison between the redox chemistry of these two classes of compounds, with special emphasis on solvent behaviour. Such a comparison should shed more light on the nature of the metal ligand bond in each series.

In 1975 Davis and co-workers [1,2] demonstrated a marked solvent dependence upon the various redox equilibria exhibited by iron and cobalt porphyrins (see Table 1). In particular, they noted that oxidation of iron(II) to iron(III) was favoured by DMSO relative to pyridine but that the reverse was true for oxidation of cobalt(II) porphyrins to cobalt(III). These workers also recognized that these solvents are axially coordinated to the metal atoms, and that five or six coordinate complexes might be formed.

Recently Kadish and co-workers [5,12] have reported more complete data

on these systems and extended the study to manganese porphyrins [4]. Some data on chromium porphyrins also exist [14,15].

Similar data for iron [18,19], cobalt [21,22], manganese [22] (Table 2) and chromium [22] phthalocyanines have now accumulated, and it may be appropriate to begin a detailed comparison of these data sets [25].

Many factors determine redox couple energies. These include coordination number, geometry and spin state of each partner, the relative binding of solvent to each partner, and whether the solvent replaces any group upon complexation, the possible binding of counter-ions, the existence or absence of ion pairing, solvation energies, solvent polarity and steric effects.

Tables 1 and 2 include phthalocyanine and porphyrin redox energies for the M(III)/M(II) couples, where M = Cr, Mn, Fe and Co, and M(II)/M(I) for M = Co and Fe, together with pertinent structural and magnetic data. Since direct magnetic measurements (static or esr) of the relevant solutions have not always been undertaken, magnetic data in Tables 1 and 2 are also deduced from solid state magnetism and from chemical experience.

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TABLE 1

METALLOPORPHYRINS - Survey of Electrochemical, Geometric and Magnetic Data as a Function of Solvent. Tetraphenylporphyrin data.

	M(III)/(II)	CN <sup>a</sup> , Mag <sup>b</sup>		M(II)/(I)	CN <sup>a</sup> , Mag <sup>b</sup>
	E <sup>o</sup> <sub>1/2</sub>	M(II)	M(III)	E <sup>o</sup> <sub>1/2</sub>	
<u>CHROMIUM</u>					
DMSO	-1.14	?	76		
<u>MANGANESE</u>					
CH <sub>2</sub> Cl <sub>2</sub>	-0.34	4 hs	5 hs		
DMSO	-0.23	6 hs	6 hs		
PYRIDINE <sup>d</sup>	-0.23	5 hs	5 hs		
<u>IRON</u>					
CH <sub>2</sub> Cl <sub>2</sub> <sup>c</sup>	-0.29	4 ls	5 ls	-1.06	4 ls
DMA	-0.11	5 hs	6 hs	-1.08	4 ls
DMSO	-0.11	76	76	-1.17	4 ls
PYRIDINE	+0.17	6 ls	6 ls	-1.48	4 ls
<u>COBALT</u>					
CH <sub>2</sub> Cl <sub>2</sub>	+0.75 <sup>e</sup>	4 ls	?	-0.855	4 ls
DMA	+0.32 <sup>e</sup>	5 ls	6 ls	-0.77	4 ls
DMSO	+0.06	5 ls	6 ls	-0.84	4 ls
PYRIDINE <sup>d</sup>	-0.37	5 ls	6 ls	-1.03	4 ls

FOOTNOTES: <sup>a</sup>Coordination number; <sup>b</sup>Magnetism - hs = high spin, ls = intermediate spin, ls = low spin; <sup>c</sup>Octaethylporphyrin; <sup>d</sup>Addition of approx. 1 molar pyridine to a poorly coordinating solvent; <sup>e</sup>Irreversible.

Supporting electrolyte is tetrabutylammonium perchlorate in most cases. Data abstracted from refs. 1 - 17. The coordination numbers and spin mentioned in these Tables are those believed to be true under the condition of the electrochemical experiment. When the solution conditions change, or in the solid state, other spin states and coordination numbers may certainly occur.



TABLE 2

METALLOPHTHALOCYANINES - Survey of Electrochemical, Geometric and Magnetic Data as a Function of Solvent.

	M(III)/M(II) $E_{1/2}^0$	M(II)	CN <sup>a</sup> , Mag <sup>b</sup> M(III)	M(II)/(I) $E_{1/2}^0$	CN <sup>a</sup> , Mag <sup>b</sup> M(I)
<u>MANGANESE</u>					
DMF	-0.138	6 1s	76 1s		
DMSO	-0.078	6 1s	76 1s		
PYRIDINE	+0.004	6 1s	76 1s		
<u>IRON</u>					
ClNap <sup>c</sup>	+0.19	74 1s	4 <sup>d</sup> 1s		
DMA	+0.377	6 1s	? <sup>d</sup>	-0.55	75
DMSO	+0.457	6 1s	? <sup>d</sup>	-0.71	5 1s
PYRIDINE	+0.661	6 1s	? <sup>d</sup>	-1.07	5 1s
<u>COBALT (TsPc)</u>					
ClNap <sup>c</sup>	+0.77	4 1s	74 1s		
DMF	+0.427 <sup>e</sup>	76 1s	6 1s	-0.497	4 1s
DMSO	+0.455	76 1s	6 1s	-0.597	4 1s
PYRIDINE	+0.040	6 1s	6 1s	-0.709	4 1s
4-Et-PYRIDINE	+0.007	6 1s	6 1s	-0.725	4 1s
3-Cl-PYRIDINE	+0.163	6 1s	6 1s	-0.638	4 1s

FOOTNOTES: <sup>a,b</sup> See table 1: <sup>c</sup> MPc from ref. [23]; <sup>d</sup> Species very unstable;

<sup>e</sup> Irreversible. All data from ref. [19,22] except for chloronaphthalene (ClNap) data.

These redox data are also presented graphically in figs. 1 and 2 as a function of the Donicity Number [26] (DN) of the solvent. In most cases, there is a remarkably good correlation between Donicity Number and  $E_{1/2}$ , whereby increasing donicity results in an almost linear increase, or decrease, in sensitivity towards oxidation, depending upon the couple concerned. Although we draw linear plots, it is evident that further data must be accumulated before their significance can be uncategorically accepted. Factors such as solvation energy and entropy, which must play a role, are obscured by such plots.

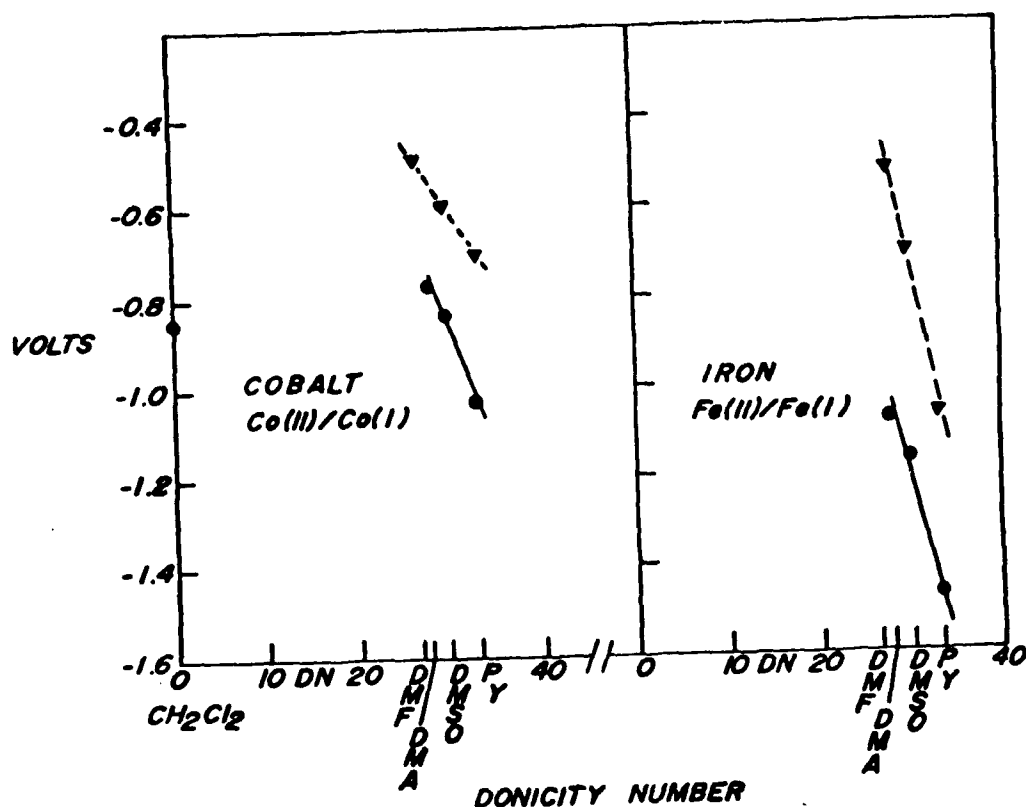


Fig. 1. A plot of the cobalt and iron(II)/(I) couples versus Donicity. The circles are tetraphenylporphyrin, the triangles (hatched lines) are phthalocyanine((Co(t-TsPc) and FePc).

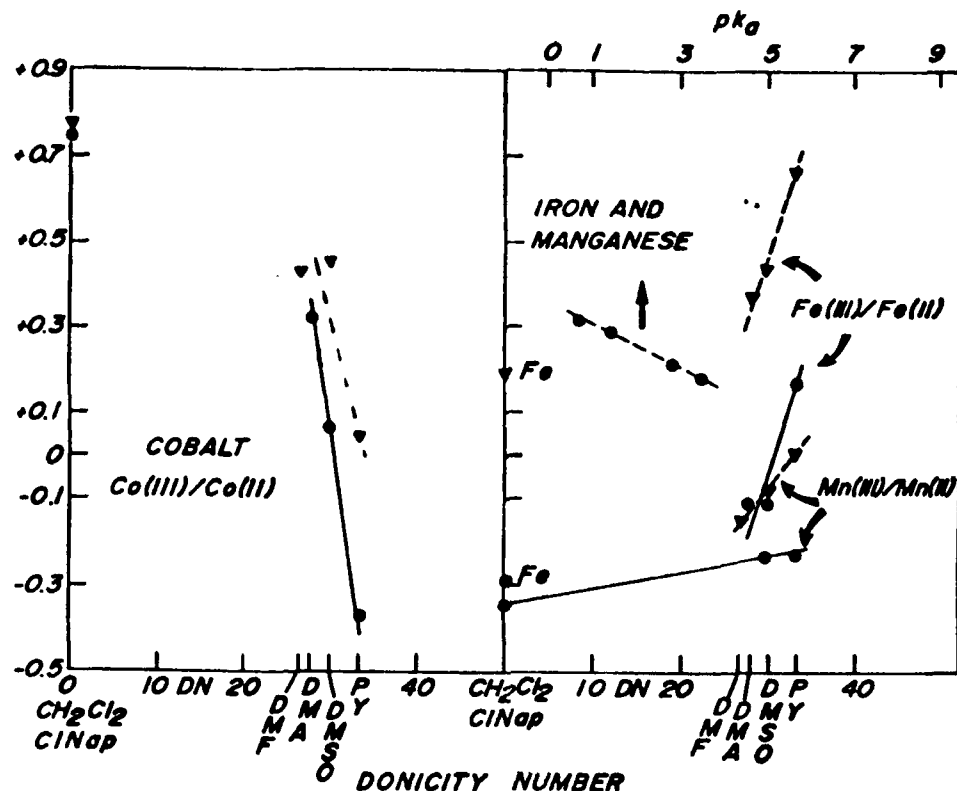


Fig. 2. A plot of iron, cobalt and manganese(III)/(II) couples versus Donicity Number. We also display a plot of the potentials for  $(X-Py)_2(TPP)Fe(III)/Fe(II)$  versus the  $pK_a$  of X-Py [12].

For all systems studied to date, a given metalloporphyrin is always easier to oxidize than the corresponding metallophthalocyanine. This may be ascribed to the smaller hole size and better  $\pi$  acceptor and poorer  $\sigma$  characteristics of the phthalocyanines relative to the porphyrins [19]. We now consider specific systems.

**Chromium:** Very little has yet been published upon chromium. It is too early to draw any conclusions save to point out the astonishingly greater stabilization of chromium(II) in the phthalocyanine series. Chromium(II) phthalocyanine can be obtained simply by dissolving hydroxy-chromium(III) phthalocyanine in pure dry pyridine under vacuo [27], yet the potential required to reduce chromium(III) octaethylporphyrin is in excess of -1.0 volts [15]: detailed solvent behaviour is not yet available.

Manganese: In general the manganese(III)/(II) potentials in both series exhibit relatively little sensitivity to solvent, with variations of only  $\pm 100$  mv. Both Mn(II) and Mn(III) porphyrins are believed to be axially coordinated by only one solvent molecule (or counter ion) and therefore five coordinate in pyridine but presumably four coordinate for Mn(II) in dichloromethane. There is some evidence that in DMSO, Mn(III) is six coordinate, i.e.  $(\text{DMSO})_2\text{Mn(III)(TPP)}^+$  [4b]. In coordinating solvents both Mn(II) and Mn(III) porphyrin species are high spin. The very small differences in potential between the dichloromethane and pyridine porphyrin systems emphasizes the relative solvent insensitivity. The phthalocyanine system is certainly low spin in pyridine [28], and presumably six coordinate. However, binding is fairly weak since the species  $\text{PcMn(II)(Py)}_2$  cannot be isolated [29].

Increasing donicity results in a stabilization of the manganese(II) state relative to Mn(III), but the effect is small (see discussion below). Both series form oxygen adducts. The greater preference for lower oxidation states in the phthalocyanine complexes provides a simple rationale for the observation of a manganese(III) phthalocyanine oxygen adduct,  $\text{PcMn(III)(O}_2^-)$  [30], compared with a manganese(IV) porphyrin oxygen adduct  $\text{TPPMn(IV)(O}_2^{2-})$  [31]. The Mn(II)/Mn(I) couple cannot be accessed prior to ring reduction.

Iron and Cobalt: The two couples Co(II)/Co(I), and Fe(II)/Fe(I) show remarkable similarity with almost the same degree of sensitivity towards solvent being expressed in both series (see figs. 1 - 3). Increasing donicity causes a relative stabilization of the higher oxidation state an effect explainable by a simple  $\sigma$  mechanism. In the cobalt case, this must be due to increasing stabilization of Co(II) since the Co(I) species is almost certainly unsolvated. Viewed from  $\text{LCo(II)S}$ , the weaker the donicity of L, the lower the energy of  $z^2$ , the more readily it will accept an electron to form  $\text{LCo(I)}$ . The same mechanism may be applied to explain the Fe(II)/Fe(I) porphyrin data. The greater  $\pi$  acidity of the phthalocyanine

unit generates a five coordinate solvent bound (S)Fe(I)pc species [19] where destabilization of the  $z^2$  electron (low spin  $d^7$ ) can contribute to the destabilization of the iron(I).

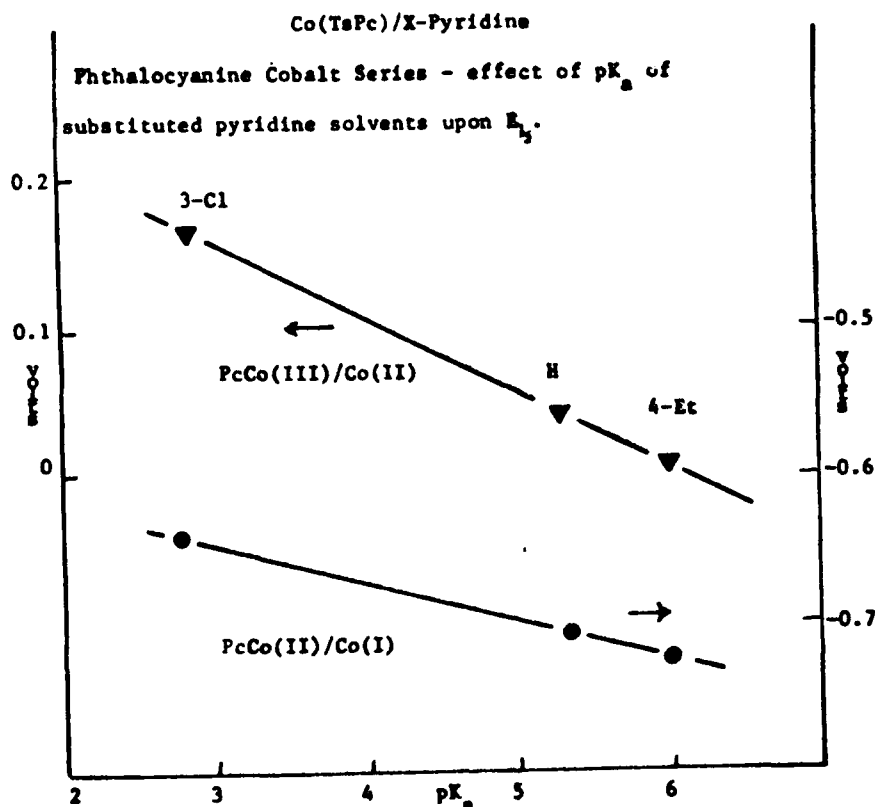


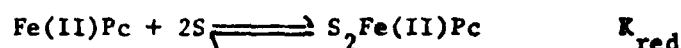
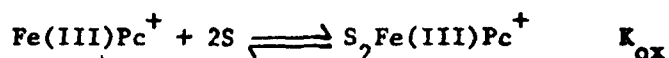
Fig. 3. A plot of  $(X-Py)_2(TsPc)Co(III)/Co(II)$  and  $(X-Py)_2(TsPc)Co(II)/(I)$  couples versus the  $pK_a$  of X-Py.

The Fe(III)/Fe(II) couple behaves in a similar fashion in both porphyrins and phthalocyanine, with increasing donicity favouring the relative stabilization of iron(II). However, in an elegant study, Kadish [12] has demonstrated an apparent reverse phenomenon when binding substituted pyridines to iron porphyrins, where the most basic pyridines favor binding to iron(III) and cause a cathodic shift in  $E_{1/2}$  (see fig. 2). Where no change in coordination number is involved, as is probably the case here,

the observed potential is given by:

$$E_{\frac{1}{2}}^s = E_{\frac{1}{2}}^{us} - \frac{0.059}{n} \log \frac{K_{ox}}{K_{red}}$$

where  $K_{ox}$  and  $K_{red}$  are the binding constants for the reactions:



and  $E_{\frac{1}{2}}^s$  and  $E_{\frac{1}{2}}^{us}$  are the standard potentials for the solvated and unsolvated species respectively. In general, binding to iron(III) will be greater than to iron(II), and both binding constants will increase with increasing  $pK_a$ . Moreover binding to the higher oxidation level will usually increase to a greater extent with increasing  $pK_a$ . The cathodic shift obtained by increasing the  $pK_a$  of the substituted pyridine is explained by this latter phenomenon.

The solvent donicity sequence requires that the ratio  $K_{ox}/K_{red}$  decreases in the sequence DMA > DMSO > Pyridine. It is not unreasonable that the soft pyridine ligand would show a greater preference for the soft iron(II) centre, than the harder oxygen ligands, and form a more covalent bond.

Invoking the E and C model of Drago [32], and assuming that entropy changes are similar for all three solvents, the data are consistent with the fact that the electrostatic component ( $E_a$ ) is similar for all three solvents, but the covalent component ( $C_a$ ) is much greater for pyridine than for the oxygen donor solvents. Increased  $\pi$  back donation in the pyridine iron(II) complex, and its synergistic effect upon  $\sigma$  bonding, enhances this covalent interaction [19]. The substituted pyridine ( $pK_a$ ) sequences in fig. 2 and 3 are a consequence of changing the  $E_a$  parameter with roughly constant  $C_a$ .

The same argument can be applied to the Mn(III)/Mn(II) system but evidently the covalent binding by Mn(II) is less important, consistent with its slightly larger size. The smaller sensitivity towards donicity in the

high spin porphyrin series, relative to the low spin phthalocyanine series probably reflects the expected decreased covalency of the high spin ions.

The cobalt(III)/cobalt(II) couple is less well behaved, and frequently yields irreversible waves. Under the conditions of the electrochemical experiment the cobalt(II) porphyrins are five coordinate, existing as low spin (S)Co(II)Por [5]. Increasing donicity causes a decreasing stabilization of cobalt(II). Unlike the iron(III)/iron(II) case, low spin cobalt(II) has a half occupied  $z^2$  orbital, i.e. configuration  $(xz,yz,xy)^6(z^2)^1$ . This  $z^2$  orbital points towards the solvent and is destabilized thereby. The conventional wisdom [7] explains the decreasing stability of cobalt(II) with increasing solvent donicity via destabilization of the  $z^2$  electron. The destabilization of  $z^2$  is a more important effect here, and in the Fe(II)/Fe(I) couple, than any arguments which might be based on changing covalency in these couples.

Esr data reveal that Co(II)Pc (e.g. tetrabutyl or tetrasulphonyl substituted) is six coordinate, low spin, in pyridine solution [36], a not uncommon coordination number for cobalt(II) phthalocyanines [37].

Fairly extensive solvent data are displayed for cobalt phthalocyanine in Table 2 and figs. 2,3. Increasing donicity causes stabilization of cobalt(II) in parallel with the porphyrin series. However, perhaps because of the irreversibility in the case of DMA, the relationship is not linear. The  $pK_a$  relationships (fig. 3) are precisely linear for both cobalt couples and reflect the change in electrostatic binding as previously observed in the iron porphyrin series by Kadish [12].

Cobalt phthalocyanine is known to form both five and six coordinate adducts [38,39]. The irreversibility in DMA may reflect the existence of (DMA)Co(II)Pc which becomes six coordinate upon oxidation. Electrochemical differences affecting both redox potential and electron transfer kinetics, as a consequence of coordination number, in the cobalt phthalocyanine series, are currently being investigated [22].

Iron(II) phthalocyanine is air stable in pure DMA, DMSO or pyridine, but oxidizes in aerated DMA containing chloride ion [19]. The latter ion causes a 500 mv cathodic shift in  $E_h$  (to -0.153 V vs sce) relative to perchlorate ion ( $E = +0.377$ ) [19]. Various oxygenated solids have been obtained by precipitation from aerated pure DMF [33] or DMSO [34], but these are presumably stabilized by lattice energy effects. Direct oxygenation occurs in pure concentrated sulphuric acid in which the ring is extensively protonated [35]. A wave at 0.4 V, in 85% sulphuric acid, is probably due to the Fe(III)/Fe(II) couple [24]. The cobalt(II) porphyrins are very air sensitive and readily form oxygen adducts. Cobalt(II) phthalocyanines are generally air stable, but do react with oxygen when cooled in non-donor solvents [39]. These observations are fully consistent with the redox behaviour of these species as interpreted in terms of the nature of the metal ligand bond.

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